

## THERMAL AND CATALYTIC COPROCESSING OF COAL AND WASTE MATERIALS

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### Introduction

Coprocessing of coal with waste materials to produce liquid fuels with emphasis on finding reasonable reaction pathways and catalysts for such processing is presently the subject of intensive investigation. Polymer wastes such as polyethylene, polystyrene, polypropylene and used rubber tires are not naturally degraded over time. More than 22 million tons of plastic waste are annually discarded in landfills and over 75 percent of used rubber tires are similarly treated.<sup>1</sup> In order to obtain distillate liquids or petroleum compatible refined products from coal, addition of hydrogen is necessary. A possible method for hydrogen addition is coprocessing of coal with polymeric waste materials since these latter materials contain hydrogen at levels much higher than are found in coal. The breakdown of waste rubber tires is interesting because the liquids derived may prove to be important as a coal dissolution and/or hydrogen donor solvent.<sup>2</sup> Recently, Badger and coworkers<sup>3</sup> reported that hydrogenated tire oils (hydrogenated in the presence of CoMo catalyst) were effective for the dissolution of coal. Studies on the coprocessing of coal and waste materials have only recently been done intensively. Limited data are available on reaction conditions and catalytic effects for processing coal mixed with post-consumer wastes. The purpose of the present study was to determine the effects of reaction temperature, pressure, catalysts, and mixture ratio on the coprocessing of coal and waste materials.

### Experimental

Blind Canyon (Utah) coal (DECS-6, -60 mesh) was obtained from the Penn State Coal Sample Bank and stored under nitrogen. Ground waste rubber tire material (-20 mesh, 0.4 % moisture, 68.7 % volatile carbon, 7.6 % ash, and 23.3 % fixed carbon) was obtained from the University of Utah Center for Microanalysis. Ground waste rubber tire was stored under air at ambient conditions. The commingled plastic mixture (mostly high density polyethylene) used in this experiment was obtained in two batches. The first batch was obtained from a recycling center in Utah (Recycling Corporation of America) in the form of detergent or soft-drink bottles. Samples were washed to remove the labels and contaminants before size reduction by cutting and shaving. Final size reduction was done by grinding in a kitchen flour mill (stainless steel) to -8 +25 mesh before analyses and use in coprocessing experiments.

The second waste plastic was obtained through the American Plastic Council (APC) from a recycling center in Oregon. Polyethylene and polystyrene were purchased from Aldrich Chemical Co. Melting and softening temperatures of some plastic polymers are given below:

<i>Plastic</i>	<i>Temperature</i>
Low Density Polyethylene	T.M. : 115° C
Mid Density Polyethylene	T.M. : 120° C
High Density Polyethylene	T.M. : 130° C
Polypropylene	T.M. : 189° C
Polystyrene	T.S. : 60-93° C

*T.M. = Melting Temperature, T.S. = Softening Temperature*

Reaction feed samples were composed of various amounts of waste plastic and rubber tire combined with Blind Canyon DECS-6 coal. When catalysts were used they were added to the mixture and their content given as a weight per cent of the solid feed material. Before reaction the feed solids were vacuum dried for two hours at 100°C. Samples were placed in glass tubes stoppered with glass wool. The glass tubes were placed in 27 cm<sup>3</sup> tubing bomb reactors, purged with nitrogen, and pressurized to 1000 psig H<sub>2</sub> (cold). Reactors were heated by a fluidized sandbath held at various reaction temperatures. The tubing reactors were shaken vertically at 160 rpm for various lengths of time, removed, and allowed to cool overnight under pressure.

Rubber tire/coal reaction products were removed and extracted with tetrahydrofuran (THF). The THF solubles were filtered to remove carbon black. The THF was removed with a rotary evaporator, and the THF soluble portion was dried under vacuum for two hours. The

sample was then extracted with cyclohexane. The cyclohexane was removed using a rotary evaporator leaving rubber tire/coal oil. The cyclohexane insoluble residue will be referred to as preasphaltenes and asphaltenes. The THF-insoluble portion is referred to as char. All product yields are calculated on a dry, ash-free, and carbon black-free basis.

Plastic/coal reaction products were removed and extracted with cyclohexane. The cyclohexane was removed with a rotary evaporator and the residue (preasphaltenes and asphaltenes) was dried under vacuum for two hours. Cyclohexane-insolubles were subsequently extracted with THF. The THF-insoluble portion is referred to as char. This char also contains any inorganic material present in the coal or waste polymer feed. Products soluble in THF were obtained using a rotary evaporator, and dried for two hours under vacuum at 100°C. All product yields are calculated on a dry, ash-free basis.

## Results

### Waste Rubber Tire Material

Figure 1 shows the breakdown of products including the total conversion, oil + gas yields, and preasphaltene/asphaltene yields for various mixtures of tire rubber and Blind Canyon DECS-6 coal coprocessed under hydrogen for one hour at 350°C with a molybdenum catalyst (ammonium tetrathiomolybdate). Total conversion values reported here are reproducible within  $\pm 2\%$ . Figure 1 suggests that as the rubber tire content of the mixture increased, so also did the oil and gas yields. Accordingly, as the tire rubber percentage decreases and coal becomes the dominant reactant, the yield of asphaltenes increases, and oil + gas yields decrease. Since tire rubber breaks down into THF soluble components quite readily, the increase of the gas and oil products and the decrease in preasphaltenes/asphaltenes with increasing tire rubber content is not surprising. The straight diagonal line is drawn on Fig. 1 to indicate the conversion expected for a tire and coal sample mixture calculated from samples consisting only of tire/catalyst and only of coal/catalyst assuming no interaction of the two reactants takes place that would inhibit or enhance total conversion. The total conversion points above the solid line show that there is some synergism for sample compositions between 10% tire rubber and 30% tire rubber by weight. It appears from the preasphaltene/asphaltene curve in Fig. 1 that this may be related to an increase in production of preasphaltenes/asphaltenes. Figure 2 presents results of further work with various mixes of tire rubber and coal with the same molybdenum catalyst but at 430°C. Again the solid line indicates a theoretical value for the total conversion based on samples consisting of only coal/catalyst liquefied at 430°C and only tire/catalyst at 430°C. It is interesting to note that the synergism which takes place at 350°C does not seem to occur at the same tire/coal composition at which synergism is observed for samples processed at 430°C. Instead, at 430°C the synergism is noted for almost all samples coprocessed. The observed synergism at 430°C also is due to an increase in yields of preasphaltenes/asphaltenes.

Coprocessing for one hour periods at 430°C is found to be more beneficial than at 350°C for enhancement of product yields (Figure 3). Table 1 shows the amount of zinc found in the oil products from coal/tire coprocessing. Samples obtained by reaction at 430°C were found to contain less zinc than samples obtained at 350°C. Higher temperatures may enhance zinc deposition in the ash or zinc scavenged by the coal, thus diminishing the amount of zinc found in the products. Such scavenging could be beneficial in eliminating the need for a secondary process to remove zinc from the coprocessing-derived oils. While processing samples at different temperatures, we have noted a difference in the amount of carbon black found in the product oils. The carbon black is thought to be unsuited to hydrotreatment. During the extraction procedure using THF, some carbon black passes through the cellulose filters into the extraction mixture. The carbon black tends to stick to the solvent extraction apparatus. We have further noted that samples coprocessed at 430°C tend to dirty the glassware less. In order to calculate conversion to products accurately the carbon black is filtered out. We then observed for some of these samples coprocessed at higher temperatures and made up of more than 50% tire rubber that less carbon black was being filtered out. Figure 4 compares the amount of carbon black that was filtered out for samples coprocessed at 350°C and 430°C. The percentage of carbon black filtered out of the THF solubles is plotted versus the composition of the tire/coal mixture. At the lower temperatures and at higher tire rubber percentages larger amounts of the carbon black passed through the cellulose filter. This result may only be related to conditions of coprocessing with a tubing reactor and the manner in which we extracted our samples, but the result may be of some use in decreasing the amount of carbon black that becomes mixed into the oil products in a commercial operation.

### Plastic Wastes

We have studied extensively the liquefaction of Blind Canyon coal, which has a low pyrite content. Hydroliquefaction of this and other coals of similar rank gives high yields of liquid products at temperatures around 350–430°C. As shown in Fig. 5, liquefaction of coal at higher temperatures results in decreased liquid yields and higher quantities of gases being produced. Maximum oil production was obtained at 430°C.

Commingled plastic wastes used in these experiments contained some polystyrene, and other plastics, but the most abundant polymer in this waste was high density polyethylene (HDPE). HDPE has the highest decomposition temperature of the plastic materials we tested (400–430°C) which made the optimum reaction temperature for processing commingled plastic higher than for coal.

From Fig. 6 (processing of commingled plastic for one hour), the maximum total conversion was reached (96%) at 430°C and higher temperatures. Oil production increased as the reaction temperature increased. Maximum oil production occurred at 430°C. Once the temperature was above 430°C the oil yield dramatically decreased as the gas production increased. Coprocessing plastic and coal together showed optimum conditions for total conversion and oil production at 430°C and a reaction time of one hour (Fig. 7).

As shown in Fig. 8, mixing plastic with coal did not result in any improvement of total conversion. Synergism was observed only for oil production for coal/plastic coprocessing. The observed synergism appears to be due to a decrease in the yield of asphaltene.

### Summary

Coprocessing at 430°C was found to give the highest total conversion yields for coal/rubber tire material coprocessing for one hour under a hydrogen atmosphere with a molybdenum catalyst. The zinc and carbon black contamination in the derived liquids was diminished when samples were coprocessed at 430°C. Coprocessing of coal with commingled plastic showed a synergistic effect on oil production but not on the total conversion.

### References

1. Franklin Associates, Ltd.; Characterization of Plastic Products in Municipal Solid Waste; Final Report February 1990; prepared for the Council for Solid Waste Solution.
2. Farcasiu, M.; Smith, C., Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem., 1992, 37 (1), 472.
3. Badger, M. W.; Harrison, G.; Ross, A. B., 1994, Prepr. Pap. Am. Chem. Soc., Div. of Petroleum Chem., 39 (3), 438.

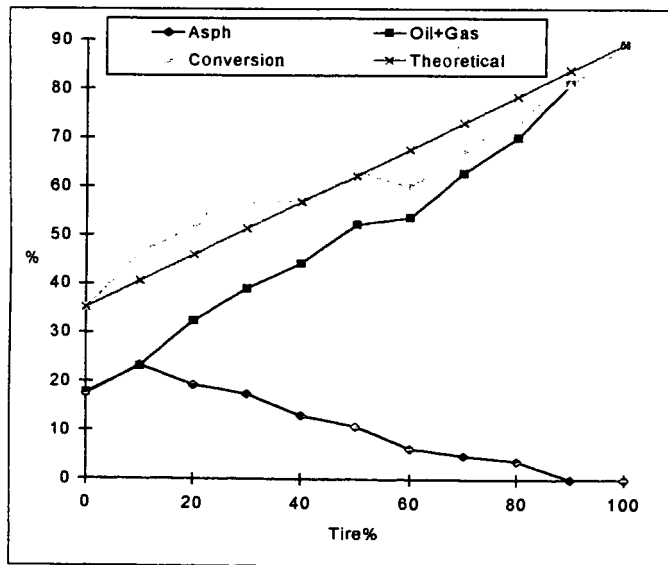


Fig. 1. Tire/coal products from coprocessing at 350 Celsius for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen with a molybdenum catalyst.

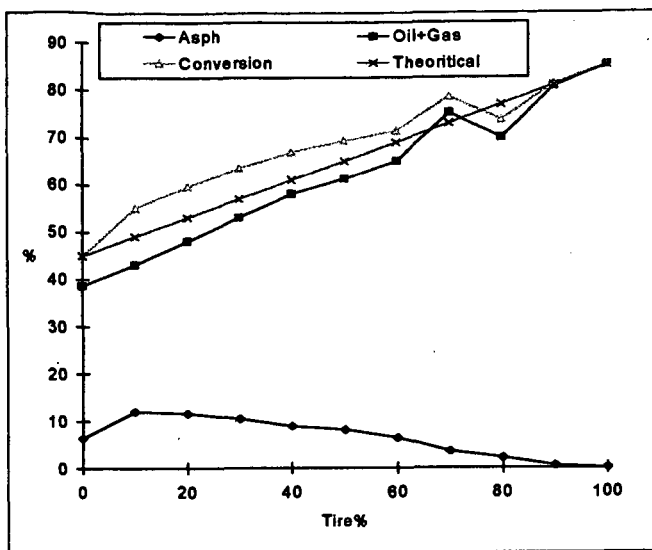


Fig. 2. Tire/coals products from coprocessing at 430 Celsius for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen with a molybdenum catalyst.

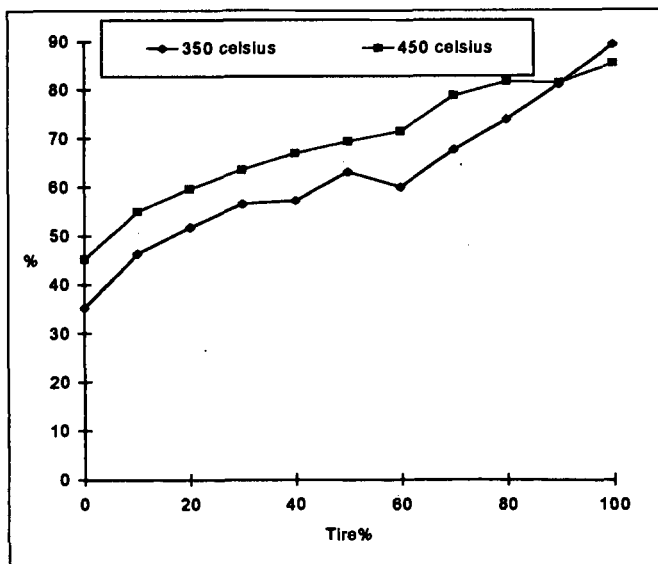


Fig. 3. Tire/coals total conversion comparison for samples coprocessed at 430 Celsius and 350 Celsius for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen with a molybdenum catalyst.

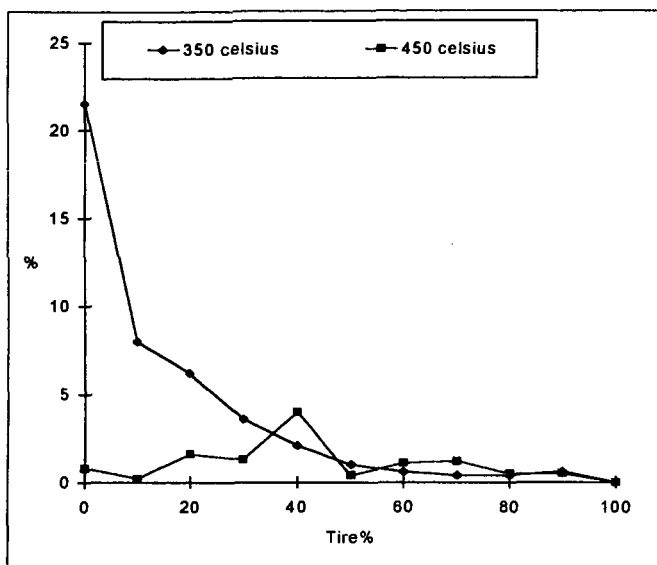


Fig. 4. Percentage of carbon black filtered out of THF soluble liquids for coal/tires samples coprocessed at 350 Celsius and 430 Celsius for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen with a molybdenum catalyst

Table 1. Percentage of zinc (by weight) in cyclohexane soluble oils obtained from coal/tire rubber samples coprocessed in tubing bomb reactors with reaction times of 1 hour under at 1000 psig (cold) hydrogen with a molybdenum catalyst.

Coal %	Tire %	350° Celsius	430° Celsius
0	100	0.017 %	0.007 %
30	70	0.016 %	0.008 %

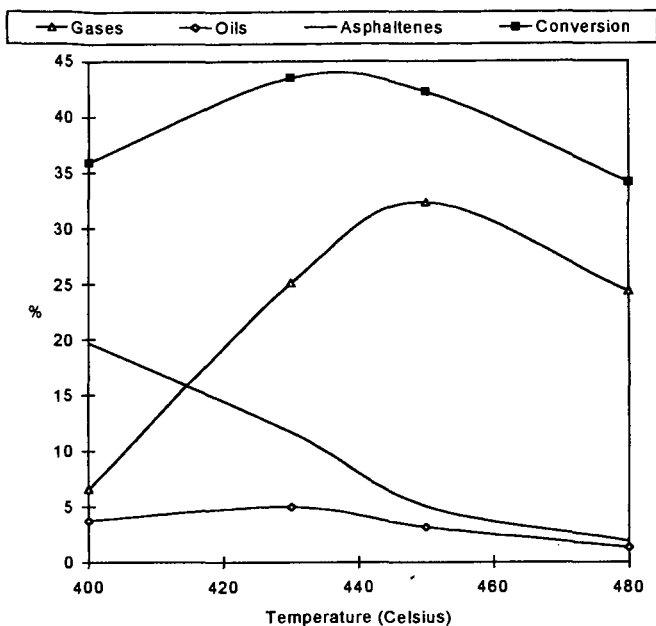


Fig. 5. Liquefaction results for DECS-6 coal hydrotreated for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen

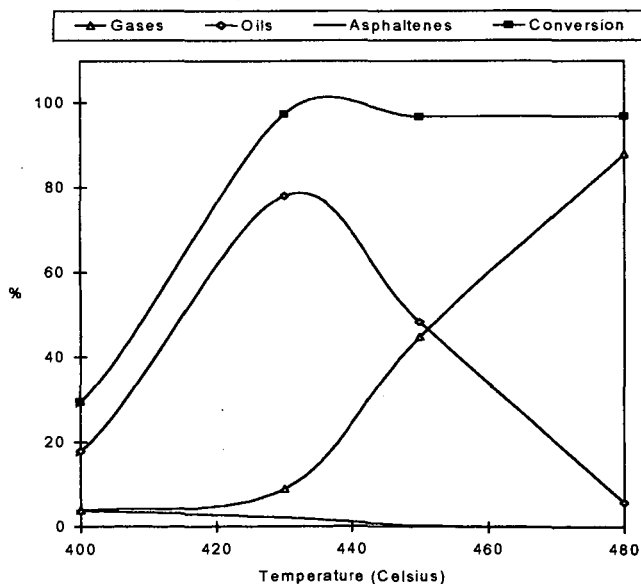


Fig. 6. Liquefaction results for commingled plastic #2 [APC] hydrotreated for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen.

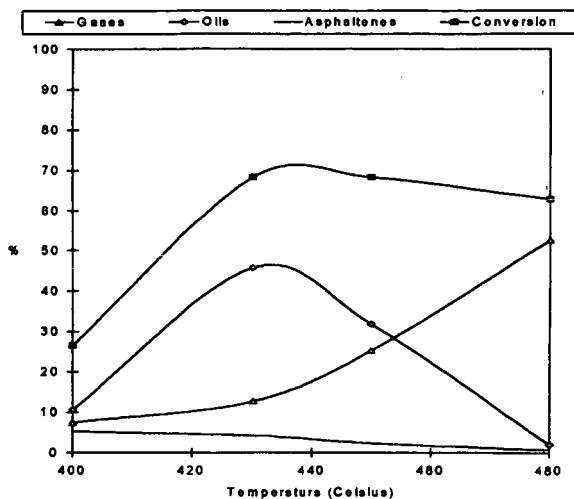


Fig. 7. Results for coprocessing of commingled plastic #2 [APC] and DECS-6 coal for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen.

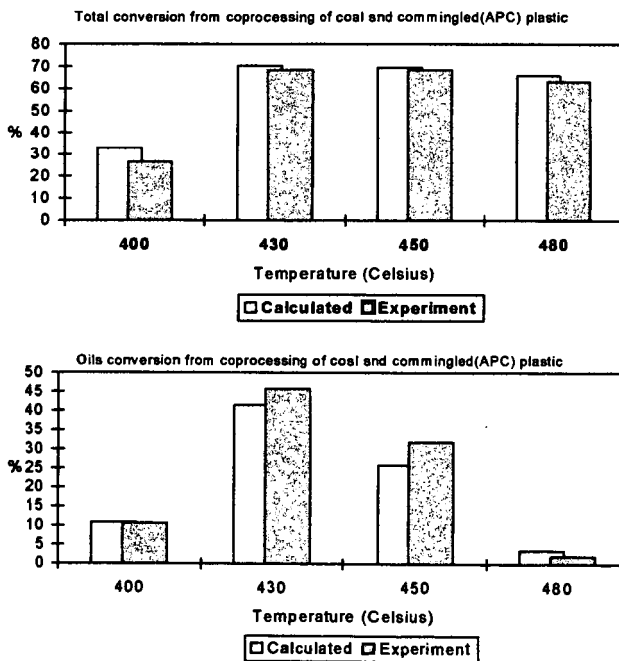


Fig. 8. Experimental and calculated results for coprocessing of commingled plastic #2 [APC] and DECS-6 coal for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen.